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GEOLIPIDS IN THE OIL SHALE FROM ALEKSINAC (YUGOSLAVIA)

By

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INTRODUCTION

The oil shale from Aleksinac (Yugoslavia) is a lacustrine sediment of Miocene age. Both the soluble portion of the organic matter (the bitumen) and the insoluble kerogen of this shale were studied extensively. In this paper, isolation and identification of various types of geolipids from the Aleksinac shale, carried out in the last few years, will be reviewed. A thorough examination of the bitumen was expected to give additional data on the origin of the organic matter as well as on the sedimentation conditions and postburial changes.

EXPERIMENTAL PROCEDURES

The shale sample contained 20.4% organic matter (1). It was powdered to -100 mesh (Tyler). In most cases, the bitumen was isolated by 100 h Soxhlet extraction either with benzene or with a mixture of benzene and methanol (1:1).

Various schemes for isolation of different fractions and various separation techniques were used, such as the usual chemical method, chromatographic techniques, molecular sieving and clathration.

Identifications were made by gas chromatography involving coinjection of internal standards, or by a system of gas chromatograph, mass spectrometer and computer.

RESULTS AND DISCUSSION

The yields of the benzene- and benzene-methanol bitumens were 1.25% and 4.27%, respectively. The bitumens consisted mainly of neutral components (Table I).

TABLE I

COMPOSITION OF THE BITUMEN

Constituents	% of the benzene-bitumen	% of the benzene-methanol bitumen
Neutral	81.36	53.48
Acids	6.51	31.46
Phenols	7.28	8.18
Basic	0.21	0.17

n-Alkanes

The n-alkane fraction was found to consist of a C_{13}-C_{37} homologous series (Figure 1) with a predominance of odd-carbon-numbered members in the C_{25}-C_{37} range (2). The CPI was 1.46 and 1.75, for the n-alkanes from the benzene- and benzene-methanol bitumen, respectively, indicating that the organic matter of Aleksinac shale was non-mature.

Branched Alkanes

Phytane and pristane, with a dominance of phytane over pristane, were found in considerable amounts. The dominance of phytane over pristane indicated a higher plant's origin of the organic matter of this sediment. Other aliphatic isoprenoid alkanes: C_{15} (farnesane), C_{16} and C_{18} were also identified in the thiourea adduct. In the thiourea adduct of the branched-cyclic fraction, a C_{18}-C_{28} series of iso- or anteiso-alkanes was suggested by gas chromatography involving coinjection of five standards of iso-alkanes. Two nonidentified homologous series containing 7 and 9 members were also found in the thiourea adduct of the branched-cyclic fraction.

Cyclic Alkanes

In the cyclic fraction, the following polycyclic isoprenoid compounds were identified: C_{27}-C_{29} steranes, methyl-C_{29} sterane, C_{27}-C_{32} pentacyclic triterpanes of hopane and lupane type (except C_{28}) and the bicyclic tetraterpane perhydro-β-carotane (Table II).

TABLE II

ISOPRENOID ALKANES IDENTIFIED IN THE ALEKSINAC SHALE BITUMEN

Aliphatic	C_{15}	C_{16}	C_{18}	C_{19}	C_{20}		
Steranes	C_{27}	C_{28}	C_{28}	C_{29}	C_{29}	C_{29}	
5 H	α	$\alpha+\beta$	?	α	α	α	
14 H	$\alpha+\beta$	β	$\alpha+\beta$	β	$\alpha+\beta$	α	
Triterpanes	C_{27}	C_{27}	C_{29}	C_{29}	C_{30}(4)*	C_{31}(3)*	C_{32}
17 H	α	?	α	?	?	?	α

* Number of isomers

All these compounds have already been known as bitumen constituents of other shales. However, the identified steranes suggest a higher plant's origin of one part of the organic matter of Aleksinac shale. On the other hand, a certain number of identified triterpanes of hopane type may have originated from lower procaryotic organisms in which hopane oxygen compounds were identified lately (3). On the basis of the presence of thermodynamically stable stereoisomers of steranes and triterpanes, nonspecific for biological molecules, such as 14βH holestane, ergostane and sitostane, 17αH, 21 βH norhopane and bishomohopane, it is possible to speculate on diagenetic and maturation changes of the organic matter of Aleksinac shale.

Aromatic Hydrocarbons

A few classes of aromatic hydrocarbons were isolated and identified (4): C_nH_{2n-14} (biphenyls) and C_nH_{2n-18} (anthracenes and/or phenanthrenes). These aromatic hydrocarbons are presumably products of diagenetic changes characteristic for most ancient sediments.

Aliphatic and Aromatic Acids

A review of various acids identified in the Aleksinac shale is given in Table III. It is obvious that similar types of aliphatic acids were found in benzene- and benzene-methanol bitumen as well as in the extract of demineralized shale and in kerogen hydrolysis product. The only difference was in the range of the members in the homologous series. The list of acids isolated from aqueous extract of the shale is given for comparison (5).

Fatty Acid Methyl Esters

In one of the polar fractions of the benzene-bitumen, methyl esters of fatty acids (C_4-C_{25}) were isolated and identified by high resolution mass spectrometry (4). As far as we know, fatty acid methyl esters had not been found earlier as biolipids or geolipids. If their existence in various shale bitumens should be confirmed, their appearance could be explained either by diagenetic transformation of some precursor biological aliphatic molecules, or they might originate from biolipids so far unknown.

Aliphatic γ- and δ-Lactones

One of the most interesting findings in one of our first investigations of the acidic fraction (6) was the identification of a homologous C_7-C_{15} series of γ-lactones in this fraction (Figure 2). It was a surprise to find a homologous series of components whose mass spectra had only one significant peak at m/z 85 (Figure 3).

The finding of γ-lactones in the bitumen of Aleksinac shale added a new structural type to the organic compounds found in geological specimens. However, the question was posed whether γ-lactones were indigenous to the organic matter of the shale and appeared in the acidic fraction from the base hydrolysis and subsequent acidification, or perhaps were produced, also during the isolation procedure, from precursors, such as the corresponding 4-hydroxy-acids of Δ-3 or Δ-4 usaturated carboxylic acids.

Therefore, in another experiment (7), the neutral fraction was isolated by a careful procedure (extraction of bitumen at room temperature and isolation of acids by weak alkali) to avoid the formation of γ-lactones during the Soxhlet extraction of the bitumen and the possible hydrolysis of γ-lactones. Since in this experiment γ-lactones were isolated in relatively high yields, 0.41% and

0.34% relative to the benzene- and benzene-methanol bitumen, respectively, it was proved that they were indigenous to the organic matter of the shale.

Samma-lactones are quite prevalent in biolipids and in microbiological transformation products. Any of these may be the source of γ-lactones. Hydroxy-acids and unsaturated acids may also be the source of γ-lactones in Aleksinac shale. If γ-lactones would be found typical for certain class of sediments, they might shed more light on the source of the organic matter of these sediments.

In addition to γ-lactones, δ-lactones were also added to the organic compounds found in geological samples (8). Mass spectrometric identification of δ-lactones was based on the fragmentation ion m/z 99. However, they were present in very small quantities and their molecular ions in the mass spectra were not particularly pronounced so that it was not possible to establish with certainty which members of the 4-member homologous series were present.

TABLE III

ACIDS IDENTIFIED IN THE ALEKSINAC OIL SHALE

Products identified	Free acids extracted with: Water plus acidification (raw shale and bitumen-free shale)	Free acids extracted with: Benzene and benzene-methanol (raw shale)	Bound acids: Kerogen (hydrolysis)	Bound acids: Entrapped (after removal of mineral part)
Aliphatic acids				
Sat. unbranched				
Monocarboxylic	--	C_6-C_{12}	C_6-C_{33}	C_5-C_{32}
Dicarboxylic	C_6-C_{15}	C_7-C_{18}	C_3-C_{30}	C_3-C_{28}
Aromatic acids				
Monocarboxylic	Benzoic Methoxy-benzoic Me-hydroxy-benzoic Hydroxy-benzoic Me-naphthoic	Benzoic Me-benzoic (2)* di-Me-benzoic (4) tri-Me-benzoic Hydroxy-benzoic (2) Methoxy-benzoic Naphthoic (2) Me-naphthoic	Benzoic Me-benzoic	
Dicarboxylic	Benzene (2) Me-benzene Hydroxy-benzene Me-hydroxy-benzene Naphthalene (2)	Benzene Me-benzene (2) Naphthalene		
Tricarboxylic	Benzene (3) Naphthalene (4)	Benzene		

* Numbers in parentheses indicate the number of isomers

Cyclic γ-Lactones

Two cyclic γ-lactones were identified, i.e. γ-lactones of 6-hydroxy-2,2,6-trimethyl-cyclohexylidene acetic acid (dihydroactinidiolide) and 6-hydroxy-2,2,6-trimethyl-cyclohexyl acetic acid (tetrahydro-actinidiolide). Figures 4 and 5 show a comparison of mass spectra obtained with reference spectra of authentic compounds from the literature (8).

It may be supposed that cyclic γ-lactones were formed by lactonization of acids which might represent intermediates in a bacterial or abiogenic oxidation of carotenoids into naphthenic acids. Corresponding acids were isolated from a Californian petroleum and it was assumed that they were formed by oxidation of β-carotene (9).

Other Polar Constituents

Several other compound types were identified in the polar fraction. In addition to isoprenoid ketones 6,10-dimethyl-undecan-2-one (C_{13}) and 6,10,14-trimethyl-pentadecan-2-one (C_{18}), which were not a novelty in the chemistry of geolipids, C_{13}-C_{24} aliphatic methyl ketones and the triterpenoid ketone adiantone were identified (4).

As far as we know, aliphatic methyl ketones as such were unknown as biolipid constituents. It may, therefore, be assumed that the aliphatic methyl ketones found in the Aleksinac shale bitumen

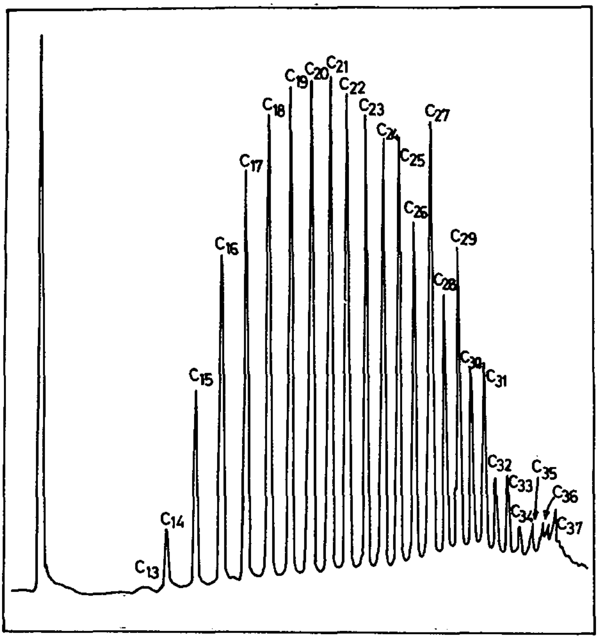

FIGURE 1. - Chromatogram of the n-Alkane Fraction of the Benzene-Bitumen.

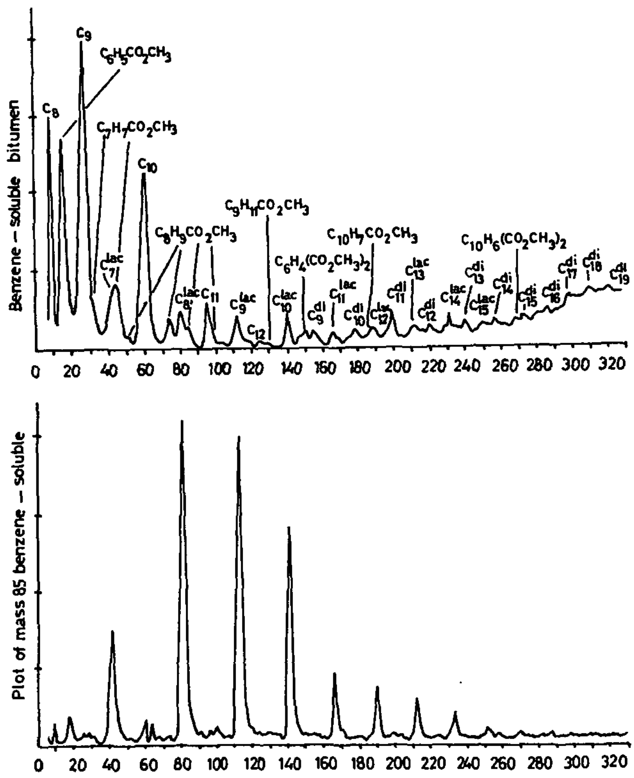

FIGURE 2. - Total Ionization Plot and Plot of Mass 85 for the Benzene Soluble Bitumen.

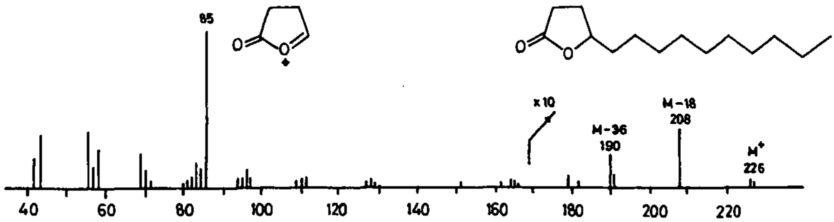

FIGURE 3. - Mass Spectrum Recorded During the GC-MS Analysis of the Lactone Mixture.

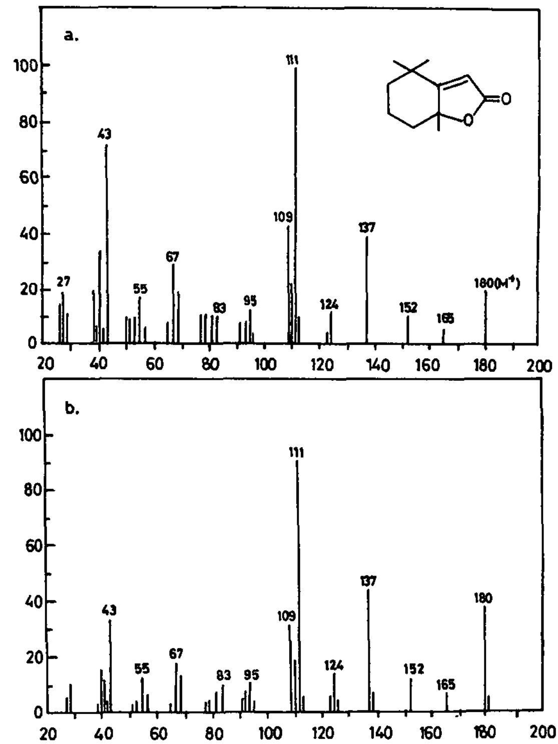

FIGURE 4. - Mass Spectrum of Authentic Dihydro-actinidiolide (a) and Mass Spectrum 5 Recorded During the GC-MS Analysis of the Lactone Mixture (b).

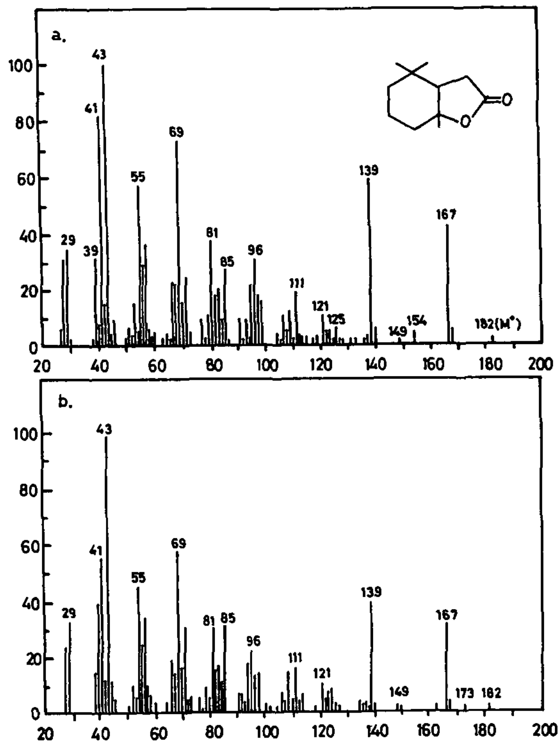

FIGURE 5.–Mass Spectrum of Authentic Tetrahydroactinidiolide (a) and Mass Spectrum 7 Recorded During the GC-MS Analysis of the Lactone Mixture (b).

are a product of microbiological oxidation of higher fatty acids or alkanes. This assumption is supported by the fact that methyl ketones have been found in soil and peat as well as in tobacco leaves dried in air and sun for two years. The bitumen of Bouxwiller shale was found to contain higher members (C_{27}-C_{36}) of this homologous series (10).

The triterpenoid ketone adiantone represents an intact biological indicator, which at the same time indicates that one part of the organic matter of Aleksinac shale originates from ferns. Adiantone is also a known constituent of Bouxwiller shale (10).

CONCLUSIONS

Most of the geolipids so far identified in the oil shale from Aleksinac represent well known and ubiquitous constituents of sediments: n-alkanes, aliphatic and cyclic isoprenoid alkanes including steranes, triterpanes and tetraterpanes and aliphatic and aromatic mono- and dicarboxylic acids. Moreover, several classes of compounds were identified which were also known as constituents of some ancient sediments but were not found to be ubiquitous, such as aliphatic isoprenoid ketones C_{13} and C_{18}, aliphatic methyl ketones C_{13}-C_{24} and the triterpenoid ketone adiantone.

However, in the Aleksinac shale bitumen geolipid constituents were identified which had not been found earlier in ancient sediments: a homologous C_7-C_{15} series of aliphatic γ-lactones, a homologous series of 4 members of δ-lactones, two cyclic γ-lactones (dihydro- and tetrahydroactinidiolide), as well as a homologous series of methyl esters of fatty acids (C_4-C_{25}).

The composition and distribution of identified geolipids suggest: a) that the Aleksinac oil shale is a non-mature sediment (relatively high content of oxygen compounds with unchanged biolipid molecules, high n-alkane CPI values, relatively high amount of unstable stereoisomers in the fraction of steranes and triterpanes) and b) that the organic matter of Aleksinac shale is of mixed origin; the following precursors of the organic substance were incorporated in this lacustrine sediment: residues of continental plants, ferns and algae, as well as residues of micro-organisms, most probably of those which took part in early diagenetic changes of sedimented organic matter.

ACKNOWLEDGMENTS

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